Enhanced Superconductivity by Rare-earth Metal-doping in Phenanthrene

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We successfully synthesized La- and Sm-doped phenanthrene powder samples and discovered superconductivity at T_c around 6 K in them. The T_cs are 6.1 K for LaPhenanthrene and 6.0 K for SmPhenanthrene, which are enhanced by about 1 K and 0.5 K compared to those in A_3Phenanthrene (A=K and Rb) and in $Ae_{1.5}$Phenanthrene (Ae = Sr and Ba) superconductors respectively. The superconductive shielding fractions for LaPhenanthrene and SmPhenanthrene are 46.1% and 49.8% at 2 K, respectively. The little effect of the doping of the magnetic ion Sm^{3+} on T_c and the positive pressure dependence coefficient on T_c strongly suggests unconventional superconductivity in the doped phenanthrene superconductors. The charge transfer to organic molecules from dopants of La and Sm induces a redshift of 7 cm^{-1} per electron for the mode at 1441 cm^{-1} in the Raman spectra, which is almost the same as those observed in A_3Phenanthrene (A=K and Rb) and $Ae_{1.5}$Phenanthrene (Ae = Sr and Ba) superconductors.

The first observation of superconductivity in a carbon-based compound traces back to 1965, when superconductivity was observed in the first stage alkali-metal intercalated graphite C_8K.[1] Up to now, the superconductors based on carbon mainly consist of three types of materials: graphite intercalation compounds (GIC), doped fullerenes, and organic compounds. For all of these carbon-based superconductors, there are commonly five-member rings or six member rings with conjugated π-orbital interactions among these rings. The π-electron can delocalize throughout the crystal, giving rise to metallic conductivity due to a π-orbital overlap between the adjacent molecules. At present, the highest-T_c superconductor for these carbon-based materials is an alkali metal-doped fullerene, namely Cs_3C_{60} under pressure ($\sim$ 12 kbar) with T_c $\sim$38 K.[3, 4] Among the organic compounds, the previous record of T_c was held by the tetrathiafulvalene derivative (BEDT-TTF)$_2$CuN(CN)$_2$Cl with T_c=12.8 K under 0.3 kbar pressure[5]. While, very recently, this record of T_c among superconducting organic materials was renewed by the patassium-doped picene (highest T_c $\sim$18K)[6] and subsequently the potassium-doped 1,2:8,9-dibenzopentacene (T_c $\sim$31 K)[7], whose pristine organic molecules compose of five and seven fused benzene rings, respectively. Alkali and alkali earth metal-doped phenanthrenes, whose pristine organic molecule phenanthrene consists of three fused benzene rings, are also found be superconducting with T_c $\sim$ 5 K[8, 9]. These discoveries of superconductivity in the materials with the fused benzene rings could open a novel broad class of hydrocarbon organic materi-

als for superconductors, and suggest the potential high-T_c superconductivity in the materials with long fused benzene rings. However, the mechanism for these organic hydrocarbons with long benzene rings still remain open. Some traces have been observed to hint an unconventional superconductivity in these materials, such as the positive pressure dependence of T_c and the existence of local spin moments in the superconducting compounds[8, 9]. More detailed work should be deeply conducted on this class of superconductors. The superconductivity in doped phenanthrene offers an good candidate for investigating the physics in such organic superconductors, due to the relatively simple molecular structure of phenanthrene. In this work, we doped nonmagnetic and magnetic rare-earth metal elements into the phenanthrene to study the effect of magnetic ions on the superconductivity. Superconductivity in this class of hydrocarbon organic materials was realized by the doping-induced charge (electron) transfer from the doped metal atoms to the molecules, which results in changes of the electronic structure and the physical properties. Our previous works demonstrated that 3 electrons are required to transfer into one phenanthrene molecule to get superconductivity. In the present letter, we doped rear-earth metals lanthanum and samarium, which are nonmagnetic and magnetic respectively, into phenanthrene to realize superconductivity, with nominal composition of La$_1$Phenanthrene and Sm$_1$Phenanthrene. Superconductivity was observed in these two compounds, with T_c equal to 6.1 K and 6.0 K for LaPhenanthrene and Sm-Phenanthrene, respectively. The superconducting shielding fraction is 46.1% in LaPhenanthrene and 49.8% in SmPhenanthrene at 2.5 K. Raman spectra show a redshift of $\sim$ 7 cm^{-1} per electron due to the charge transfer, which is almost the same as those in A_3Phenanthrene

(A=K and Rb) and $Ae_{1.5}$Phenanthrene (Ae=Ba and Sr) as well as that in A_3C_{60} (A=K and Rb). The pressure dependence of superconductivity in LaPhenanthrene shows a positive coefficient $d(T_c/T_c(0))/dP$ with the superconductive shielding fraction almost unchanged.
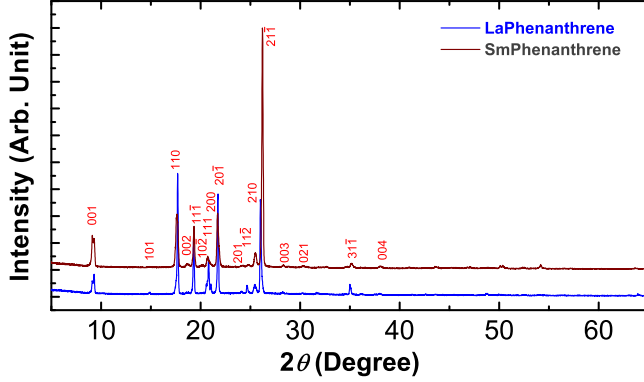

FIG. 1: X-Ray diffraction patterns for the superconducting LaPhenanthrene and SmPhenanthrene. The LaPhenanthrene and SmPhenanthrene crystallizes into the same structure as the pristine phenanthrene with space group $P2_1$.

The phenanthrene(98%) was purified by sublimation method [8]. Lanthanum(99.99%) and samarium(99.99%) were ground into powder with file and mixed carefully with the purified phenanthrene in molar ratio of 1:1 respectively. The synthesis of LaPhenanthrene and Sm-Phenanthrene is quite similar to the processes for Ba- and Sr-doped phenanthrene [9]. The mixture of rare-earth metal and phenanthrene was sintered at 240°C with the multiple-middle-treating process for totally 8 days. Finally, the products with uniform dark black color were obtained. The X-ray diffraction and Raman measurement were carried out by sealing the samples in capillaries made of special glass No. 10 and purchased from Hilgenberg GmbH. X-ray diffraction pattern was obtained in the 2-theta range of 5°C65° with a scanning rate of 0.5° per minute. Raman-scattering experiments were conducted by using the 780-nm laser line in the DXR Raman Microscope (Thermo Scientific). The scattering light was captured by using a single exposure of the CCD with a spectral resolution of 1 cm^{-1}. Low-temperature Raman spectra were performed on a Raman Microscope (Horiba JY T64000) equipped with Janis ST-500 Microscopy cryostat.

Figure 1 shows the X-ray diffraction (XRD) patterns of the La- and Sm-doped phenanthrene. The pristine phenanthrene crystallizes in the space group of P_{21}.[8, 10] The lattice parameters for the pristine phenanthrene are $a = 8.453$Å, $b = 6.175$Å, $c = 9.477$Å and β=98.28°.[8, 10] All the reflections in the XRD patterns shown in Fig. 1 can be well indexed with the space group of $P2_1$ as that for the pristine phenanthrene, just the same as previously reported alkali and alkali-earth metal-doped

phenanthrene. No impurity phase was found in the XRD patterns. From the XRD patterns shown in Fig. 1, lattice parameters are obtained as $a = 8.481$ Å, $b = 6.187$Å, $c= 9.512$Å, $\beta = 97.95$° for LaPhenanthrene and $a = 8.475$Å, $b = 6.180$Å, $c = 9.505$Å, $\beta = 98.10$° for SmPhenanthrene. The lattice parameters change slightly relative to the pristine phenanthrene. The unit cell volume expands from 489.5 $Å^3$ for the pristine phenanthrene to 494.3 $Å^3$ for LaPhenanthrene and 492.9 $Å^3$ for SmPhenanthrene. The expansion of the unit cell is similar to the previous alkali-earth metal-doped case. The smaller unit cell of SmPhenanthrene relative to LaPhenanthrene is consistent with the smaller ion radius of Sm^{3+} than that of La^{3+}.
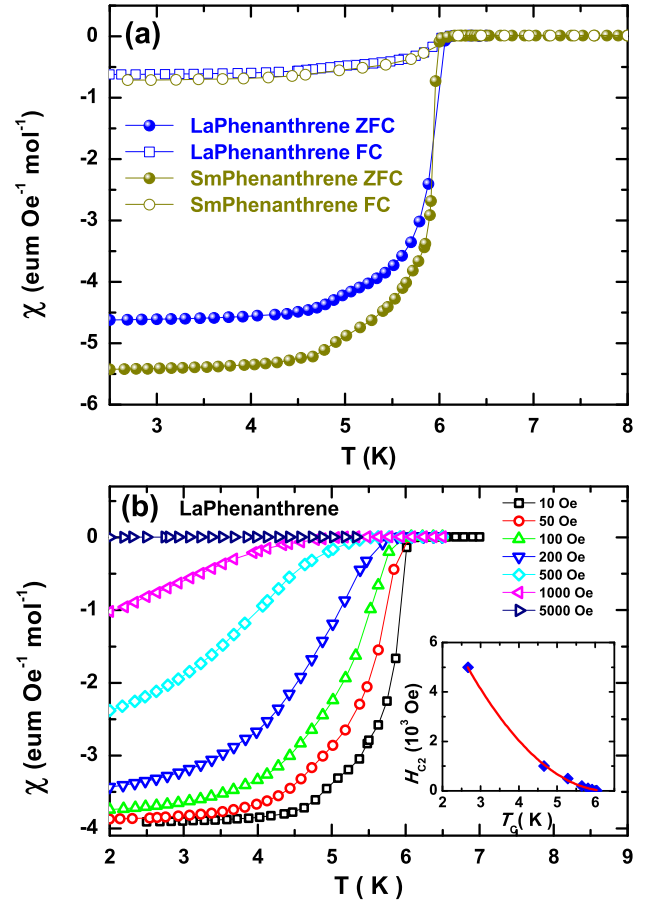

FIG. 2: Temperature dependence of magnetic susceptibility (χ) for LaPhenanthrene and SmPhenanthrene. (a). χ plotted against T for LaPhenanthrene and SmPhenanthrene in the zero-field-cooling (ZFC) and field-cooling (FC) measurements under the magnetic field of 10 Oe. (b). Magnetic susceptibility as a function of temperature for LaPhenanthrene in the ZFC measurements under different magnetic fields. The H versus T_c is plotted in the inset of (b).

Superconductivity of the LaPhenanthrene and Sm-Phenanthrene powder samples was characterized by magnetic susceptibility measurements at low magnetic field
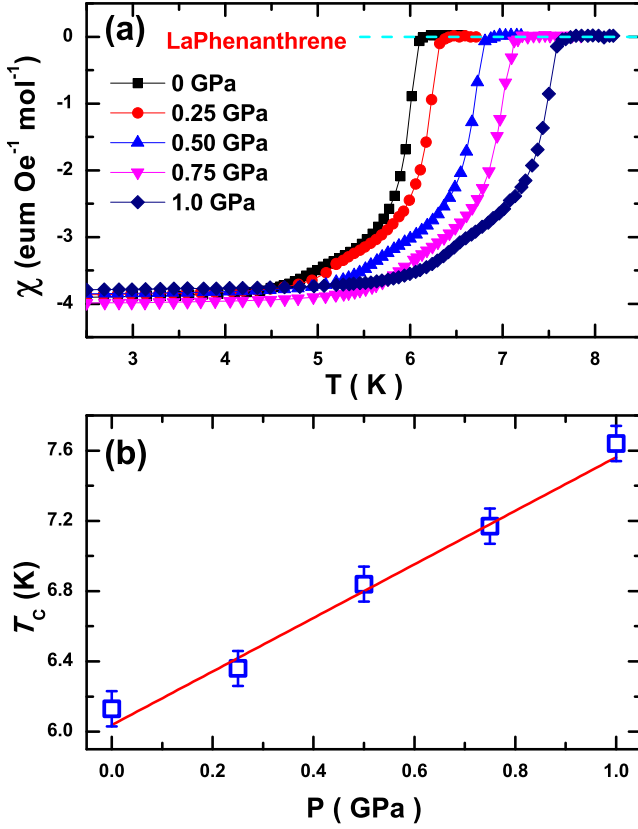
FIG. 3: Pressure dependence of superconducting transition temperature T_c for LaPhenanthrene. (a). Magnetic susceptibility plotted against T in ZFC measurements for LaPhenanthrene under the pressures of $P = 0$, 0.25, 0.6, 0.8 and 1.0 GPa. (b). T_c plotted as a function of pressure for the superconducting LaPhenanthrene.

in zero-field-cooling (ZFC) and field-cooling (FC) processes. Figure 2(a) displays the temperature dependence of magnetic susceptibility $\chi(T)$ measured in the ZFC and FC processes and under the magnetic field of 10 Oe for the powder samples of LaPhenanthrene and SmPhenanthrene. $\chi(T)$s exhibit clear and sharp drops in ZFC and FC measurements for both LaPhenanthrene and SmPhenanthrene at the temperatures of 6.1 K and 6.0 K, respectively. The temperature for the beginning of the sharp drop is defined as the superconducting transition temperature (T_c). Diamagnetic signals from ZFC and FC measurements can be assigned to superconductive shielding and Meissner effect. As shown in Fig.2(a), the shielding fraction and the Meissner fraction are 46.1% and 6.3% for the powder sample of LaPhenanthrene, 49.8% and 6.5% for the sample of SmPhenanthrene, respectively. The shielding fraction is much larger than that of alkalimetal doped picene [6] and phenanthrene [8]. The T_cs for these two rare-earth metal-doped phenanthrene are slightly higher than those of alkali metal-doped (less than 5 K) and alkali-earth metal-doped phenanthrene (~ 5.5 K), respectively.

Temperature dependence of the magnetic susceptibility of the LaPhenanthrene superconductor was measured under different magnetic fields in ZFC processes, as displayed in Fig. 2(b) . The diamagnetic signal becomes smaller and the superconducting transition gets broader with increasing the magnetic field. Superconducting transition can still be observed at 2.7 K under the magnetic field of 5000 Oe. When the field is higher than 8000 Oe, no superconducting transition is observed down to 2 K in magnetic susceptibility. The relationship between T_c and the applied magnetic field H is plotted in the inset of Fig.2(b). It is difficult to precisely determine the zero-temperature-limiting upper critical field $H_{C2}(0)$ from H-T_c plot, but it must higher than 5000 Oe.

Figure 3(a) shows the magnetic susceptibility of LaPhenanthrene in ZFC measurements as a function of temperature at different pressures up to 1 GPa. The superconducting transition temperature increases from 6.1 K to 7.6 K as the pressure increases form ambient pressure to 1 GPa while remain the magnitude of the diamagnetic signal almost unchanged. Figure 3(b) exhibits the pressure dependence of T_c. From Fig. 3(b), the temperature dependence coefficient of T_c, $\mathrm{d}(T_c(P)/T_{c(0)})/\mathrm{d}P$, can be estimated as $\sim 0.25 \mathrm{GPa}^{-1}$. This value is nearly the same as those in $Sr_{1.5}$Phenanthrene (~ 0.21 GPa^{-1}) and in $Ba_{1.5}$Phenanthrene (~ 0.23 GPa^{-1}),[9] and in K_3Phenanthrene (~ 0.26 GPa^{-1}).[8] The positive pressure effect of T_c is the common feature in the doped phenanthrene superconductors. In BCS theory, the suppression effect of T_c is expected as an external pressure is applied because the external pressure compresses the crystal lattice and consequently reduces the density of states at the Fermi level. Therefore, the unusual positive pressure effect of T_c in the doped phenanthrene superconductors could be a strong evidence for unconventional superconductivity in the doped phenanthrene superconductors.

The temperature dependence of the magnetic susceptibility measured at 5 T for LaPhenanthrene and SmPhenanthrene powder samples is displayed in Fig. 4. Curie-Weiss-like behavior is observed at high temperature for both samples, indicating the existence of local spin moments. Especially, for the SmPhenanthrene, there is an antiferromagnetic transition happening at $T_N \sim 15$ K, which is ascribed to the antiferromagnetic ordering of Sm^{3+} ions. This T_N is close to that in the elemental Sm (14.8K).[13] But no reflection for elemental Sm can be recognized in the XRD pattern shown in Fig. 1. Actually, T_N for Sm^{3+} ions can vary from several kelvins to higher than 20 K, which strongly depends on concrete compounds.[14–16] While it was reported that no magnetic order is formed for Sm^{3+} ions In $Sm_{2.75}C_{60}$.[17] One can find that the existence of the magnetic Sm^{3+} ions with antiferromagnetic order has negligible suppression effect on the superconductivity. It strongly suggests the unconventional nature of the super-
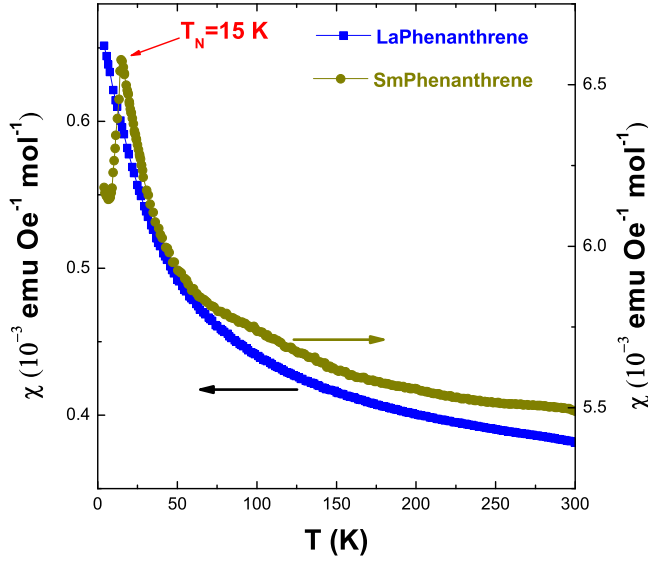
FIG. 4: High-field magnetic susceptibility for the superconducting LaPhenanthrene and SmPhenanthrene.

conductivity in the system.

As one knows, the effect of charge transferring into the fused hydrocarbon rings can be studied by Raman spectroscopies. Figure 5(a) shows the Raman spectra at room temperature for the pristine phenanthrene, LaPhenanthrene and SmPhenanthrene. As reported previously, seven major peaks can be observed in the pristine phenanthrene: 1524, 1441, 1350, 1037, 830, 411 and 250 cm^{-1}. All of these major peaks of the Raman spectrum can classified to A_1 mode, which arises from the C-C stretching vibrations[18, 19]. Clear downshift can be observed for the peaks in the Raman spectra of LaPhenanthrene and SmPhenanthrene, relative to those of the pristine phenanthrene. Such phonon-mode softening effect is attributed to the charge transfer from dopants of La and Sm atoms into phenanthrene molecules, which has been widely observed in the doped fullerenes.[20] Kato et al. pointed out theoretically that in monoanion of phenanthrene the stretching A_1 mode of 1434 cm^{-1} strongly couples to the a_2 lowest unoccupied molecular orbital (LUMO).[21] This suggests that this peak (1441 cm^{-1} in the pristine phenanthrene) can be most affected by charge transfer to the molecules and the downshift wavenumber for one electron transfer is 7 cm^{-1}. For the present two rare-earth metal-doped phenanthrene superconductors, this A_1 mode of 1441 cm^{-1} in the pristine phenanthrene moves to 1420 cm^{-1} in LaPhenanthrene and 1419 cm^{-1} in SmPhenanthrene. Consequently, the electron transfer from rare-earth metal atoms to the phenanthrene molecules induces redshifts of 21 and 22 cm^{-1} in Raman spectra for LaPhenanthrene and SmPhenanthrene respectively, which corresponds to redshift of about 7 cm^{-1} per electron in both samples. This value of redshift per electron transfer is consistent with
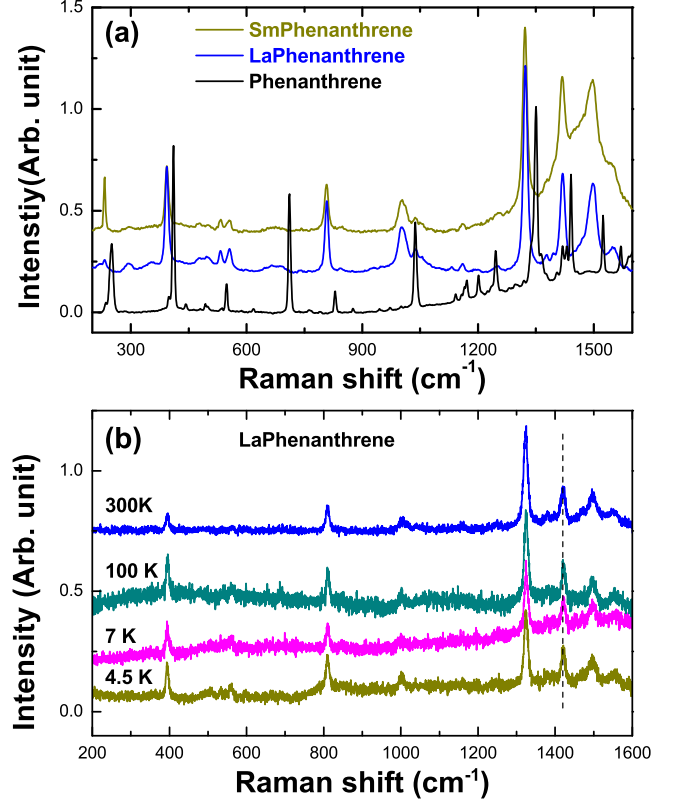

FIG. 5: (a) Raman spectra taken at room temperature for the pure phenanthrene, the superconducting LaPhenanthrene and SmPhenanthrene. (b) Raman spectra for LaPhenanthrene taken at different temperature.

those observed in the alkali and alkali earth metal-doped phenanthrene superconductors (6-8 cm^{-1} per electron) and also consistent with the theoretical prediction by Kato et al..[21] Temperature dependent measurements of Raman scattering were also performed for LaPhenanthrene at the temperatures ranging from 300 K to 4.5 K. The selected Raman spectra are displayed in Fig. 5(b). Normally, phonon anharmonicity gives rise to the following temperature dependence of the linewidth (full width of half-maximum) Γ and mode frequency ω:[22]

$$\Gamma(T) = \gamma + \Gamma_0 \left(1 + \frac{2}{e^{2\hbar\omega_0/k_B T} - 1} \right) \qquad (1)$$

$$\omega(T) = \omega_0 + C \left(1 + \frac{2}{e^{2\hbar\omega_0/k_B T} - 1} \right) \qquad (2)$$

where $\hbar\omega_0$ is the phonon frequency, k_B is the Boltzmann constant, and C is a constant. In Fig. 5(b), no shift more than 0.5 cm^{-1} can be observed for both linewidth and mode frequency with the variation of the temperature from 300 K to 4.5 K, indicating an unusual phonon decay with decreasing temperature. The nearly temperature independent $\Gamma(T)$ suggests $\Gamma_0 \ll \gamma$ so that lattice

anharmonicity is no long a dominant mechanism of the phonon decay in the present studied LaPhenanthrene. The mechanism for this unusual process of phonon decay has not been understood yet. The interactions of phonon with other excitations (for instance, electrons in conducting materials), might affect the phonon lifetime and contribute to the phonon linewidth $\Gamma(T)$ because additional channels for phonon decay could be opened by them. More measurements with higher resolution must be done to explain the temperature-independent linewidth and mode frequency. It should also be pointed out that, as seen from Fig. 5b, the Raman spectrum exhibits no obvious change as temperature cools down across T_c. However, all of these mode frequencies are much larger than $2\Delta \sim 15$ cm^{-1} (assume a BCS gap energy $2\Delta = 3.53k_{\mathrm{B}}T_c$) and so that most of these modes are not expected to be sensitive to the superconducting transition.

In summary, we successfully fabricated the new superconductors LaPhenanthrene and SmPhenanthren, which show $T_c = 6.1$ and 6.0 K, respectively. The positive pressure effect on T_c was observed in LaPhenanthrene. Especially, the antiferromagnetic order from the magnetic ion Sm^{3+} has negligible effect on T_c in SmPhenanthren. These results strongly suggest unconventional superconductivity in the doped phenanthrene-type superconductors.

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